

Hydrogen supersymmetry: A new method in perturbation theory

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Abstract

The $O(4)$ supersymmetry of the hydrogen atom is utilized to construct a complete basis using only the bound state wave functions. For a large class of perturbations, an expansion of the electron (exciton) wave function into such a complete set reduces the perturbed Schrödinger equation to a standard eigenvalue problem with an equidistant unperturbed spectrum. A high-order polarizability of the ground state of the hydrogen atom in a static electric field is calculated via Rayleigh-Schrödinger perturbation theory for illustration of the new method.

I. INTRODUCTION

The task of the perturbation theory is to calculate, at least approximately, the energy spectrum and the wave functions of the given problem using those of the already solved primary problem. As a rule, the spectrum of the primary problem consists of discrete and continuum states. Both of them should be taken into account in the expansion of the perturbed wave function. However, in practice the inclusion of the continuum is often an extremely complicated task. This is the case, for instance, of the hydrogen problem, where the bound state wave functions do not constitute a complete set even approximately: Some of the scattering states are energetically close to the bound ones, since the levels thickening point of the latter meets the continuum onset.

In the present paper we show explicitly that a specific inhomogeneous coordinate scaling applied to the hydrogen bound-state wave functions converts them into a complete set. Early in 1935 it was shown by V.A. Fock that due to the hidden symmetry of the Coulomb potential (which leads to the additional spectrum degeneracy) the three-dimensional (3D) hydrogen problem in the momentum space can be one-to-one mapped onto a sphere or onto a two-sheeted hyperboloid in 4D space, for bound or scattering states, respectively.¹ The full space of the hydrogen eigenfunctions is thus divided into two subspaces, the eigenfunctions of each subspace being an irreducible representation of the corresponding symmetry group. In particular, the bound-state wave functions are transformed into the hyperspherical harmonics, the irreducible representation of the rotational symmetry group $O(4)$ in the 4D energy-momentum space.²

An expansion into the complete basis of hyperspherical harmonics (also referred to as Sturmian functions – in the coordinate representation) has been already used in nuclear physics when treating a three-body problem (see, e.g., Refs 3,4) and recently in anisotropic exciton problem,⁵ when the perturbation theory was constructed on a sphere in 4D space. In the present work we formulate the perturbation theory directly in the coordinate space, basing on the complete set of functions orthogonal with the weight $1/r$. The important feature of this basis is that only *normalizable* (square integrable) wave functions, which belong to the bound states of the perturbed problem, can be expanded. Due to the energy-dependent transformation of the standard Coulomb wave functions which makes the basis complete, the Schrödinger equation is reduced to the eigenvalue problem with equidistant

unperturbed energy spectrum. Finally, the Brillouin-Wigner perturbation theory converges for any perturbation which only renormalizes the Coulomb spectrum leaving a set of bound states therein. The classical example of such a perturbation is the anisotropic exciton Hamiltonian. In spite of its apparent simplicity and enduring interest, the exact approach to the anisotropic exciton problem based on the present method was developed only recently.⁵ In other approaches the expansion of the wave function into an incomplete basis (see, e.g. Ref. 6) led to substantial deviation in numerical results compared to the exact method, at least for rather strong anisotropy.⁵ Nevertheless, in this work we do not dwell into details of concrete physical examples but only formulate the general recipe how to treat such kind of problems.

As soon as the perturbation leads to drastic changes of the spectrum, such as decay of formerly bound states, Brillouin-Wigner perturbation theory is not convergent any more and the solution of a truncated eigenvalue problem becomes meaningless. However, finite orders of Rayleigh-Schrödinger perturbation theory still may have some physical meaning. This is the case, e.g., of the hydrogen atom (or Wannier exciton) in a static electric field which makes the bound states of an electron (exciton) metastable, showing up in the time decay of the wave functions. At the same time, the polarizability of an atom or an exciton is described by the second perturbation order.⁷ To illustrate how the method works in such situations we calculate a high-order polarizability of the ground state in a static electric field.

II. CONSTRUCTION OF THE COMPLETE BASIS

The Schrödinger equation of the hydrogen atom has the form

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r} - E\right)\psi(\mathbf{r}) = 0, \quad (1)$$

where E , \mathbf{r} , μ , and e are the electron energy, coordinate, mass, and the elementary charge ($e > 0$), respectively. Following Fock,¹ let us introduce for the bound states $E < 0$ the energy-dependent parameter

$$a = \frac{1}{2}\sqrt{\frac{\hbar^2/2\mu}{-E}} \quad (2)$$

and make the following coordinate transformation $\boldsymbol{\rho} = \mathbf{r}/a$, where $\boldsymbol{\rho} = \rho \cdot (\sin\theta \cos\varphi, \sin\theta \sin\varphi, \cos\theta)$. Then, introducing a new wave function as $\phi(\boldsymbol{\rho}) \propto \sqrt{\rho}\psi(\mathbf{r})$,

we result in the following differential equation

$$\left\{ -\frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{1}{\rho} \left[\frac{1}{4} - \hat{\Lambda}(\theta, \varphi) \right] + \frac{\rho}{4} - \lambda \right\} \phi(\boldsymbol{\rho}) = 0, \quad (3)$$

where $\hat{\Lambda}(\theta, \varphi)$ is the angular part of the Laplace operator,

$$\lambda = 2 \frac{a}{a_B} = \sqrt{\frac{\hbar^2 / 2 \mu a_B^2}{-E}} \quad (4)$$

is a new dimensionless eigenvalue which originates from the Coulomb term in Eq. (1), $a_B = \hbar^2 / \mu e^2$ is the Bohr radius.

Equation (3) has the following eigensolutions⁸

$$\phi_{nlm}(\boldsymbol{\rho}) = y_{nl}(\rho) \mathcal{Y}_{lm}(\theta, \varphi), \quad (5)$$

where \mathcal{Y}_{lm} are the standard spherical harmonics, $\{y_{nl}\}$ is the orthogonal set of functions

$$y_{nl}(\rho) = \sqrt{\frac{(n-l-1)!}{(n+l)!}} \rho^{l+1/2} e^{-\frac{\rho}{2}} L_{n-l-1}^{2l+1}(\rho) \quad (6)$$

normalized as

$$\int_0^\infty d\rho y_{n'l}(\rho) y_{nl}(\rho) = \delta_{nn'}, \quad (7)$$

L_p^q are the generalized Laguerre polynomials (for definition see, e.g., Ref. 8), (n, l, m) are the standard hydrogen quantum numbers. The eigenvalues of Eq. (3) have the following form⁹

$$\lambda_{nlm}^{(0)} = n, \quad n = 1, 2, \dots, \quad (8)$$

leaving the same degeneracy as of the usual hydrogen spectrum. Accordingly, the scaling parameter a depends on the principle quantum number as $a = n a_B / 2$ that finally results in the standard Coulomb wave functions, normalized solutions of Eq. (1),

$$\psi_{nlm}^C(\mathbf{r}) = \sqrt{\frac{n a_B}{2r}} \phi_{nlm} \left(\frac{2\mathbf{r}}{n a_B} \right). \quad (9)$$

Being the full solution of the radial wave equation following from Eq. (3), the set of functions $\{y_{nl}(\rho)\}$, Eq. (6), also referred to as Sturmian basis,³ constitutes a complete basis in the one-dimensional ρ -space. At the same time, the spherical harmonics \mathcal{Y}_{lm} are the complete set of functions on a sphere. Consequently, the product of these two, the functions $\phi_{nlm}(\boldsymbol{\rho})$, Eq. (5), although they are not orthogonal to each other, make up a complete set in

the three-dimensional $\boldsymbol{\rho}$ -space. If we now treat a as a *constant parameter*, one and the same for all ϕ_{nlm} , we will result in the complete set of functions in the electron coordinate space,

$$\chi_{nlm}(\mathbf{r}; a) = \frac{1}{\sqrt{ra}} y_{nl}(r/a) \mathcal{Y}_{lm}(\theta, \varphi) = \sqrt{\frac{2}{naa_B}} \psi_{nlm}^C\left(\frac{na_B}{2a}\mathbf{r}\right), \quad (10)$$

normalized as

$$\int \frac{d\mathbf{r}}{r} \chi_{\nu}^*(\mathbf{r}; a) \chi_{\nu'}(\mathbf{r}; a) = \delta_{\nu\nu'}, \quad \nu = (n, l, m). \quad (11)$$

Looking at the basic functions Eq. (10) one can notice that, contrary to the Coulomb wave functions, all χ_{ν} have one and the same exponential decay factor $e^{-r/2a}$, the remainder being a set of orthogonal polynomials of r . Any square-integrable function, which decays at $\mathbf{r} \rightarrow \infty$, can be expanded into the set $\{\chi_{\nu}(\mathbf{r}; a)\}$.

III. FORMULATION OF THE BRILLOUIN-WIGNER PERTURBATION THEORY

Let us now consider the Schrödinger equation with a perturbation \hat{U} which can in principle contain differential and/or integration operators,

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{r} + \hat{U}(\mathbf{r}) - E \right] \Psi(\mathbf{r}) = 0. \quad (12)$$

Expand the wave function as

$$\Psi(\mathbf{r}) = \sum_{\nu} C_{\nu} \chi_{\nu}(\mathbf{r}; a). \quad (13)$$

Let's define again the basic parameter a as in Eq. (2) with E being now the energy of the perturbed state. Then we have

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{r} - E \right) \chi_{\nu}(\mathbf{r}; a) = \frac{\hbar^2}{2\mu a} (n - \lambda) \frac{1}{r} \chi_{nlm}(\mathbf{r}; a), \quad (14)$$

where λ is defined by Eq. (4).

Plugging Eq. (13) into Eq. (12), using Eq. (14) and the orthogonality condition Eq. (11), after convolution with $\chi_{\nu'}$ we result in the following matrix equation

$$\sum_{\nu'} \left[n\delta_{\nu\nu'} + V_{\nu\nu'} \right] C_{\nu'} = \lambda C_{\nu}, \quad (15)$$

with the unperturbed spectrum defined by Eq. (8) and the perturbation matrix

$$V_{\nu\nu'} = \frac{2\mu a}{\hbar^2} \int \chi_{\nu}^*(\mathbf{r}; a) \hat{U}(\mathbf{r}) \chi_{\nu'}(\mathbf{r}; a) d\mathbf{r}. \quad (16)$$

At first glance, Eq. (15) looks like a generalized eigenvalue problem, since the definition of $V_{\nu\nu'}$ contains the energy-dependent parameter a , and it seems that it cannot be solved by means of the direct diagonalization of the effective Hamiltonian. However, it is easily seen that any perturbation \hat{U} can be considered as an operator which is governed by a set of physical parameters $\alpha_1, \alpha_2, \dots$, such as external field strength, anisotropy degree, coupling constant, and so on: $\hat{U}(\mathbf{r}; \alpha_1, \alpha_2, \dots)$. After the coordinate transformation $\mathbf{r} = \boldsymbol{\rho}a$ it can be rewritten as

$$\frac{2\mu a^2}{\hbar^2} \hat{U}(\mathbf{r}; \alpha_1, \alpha_2, \dots) = \hat{V}(\boldsymbol{\rho}; \beta_1, \beta_2, \dots), \quad (17)$$

where the operator \hat{V} does not depend explicitly on a but is a function of new parameters $\beta_i = \beta_i(a; \alpha_1, \alpha_2, \dots)$, which, in turn, depend on a . The matrix elements Eq. (16) now take the form [see the definition of ϕ_ν , Eq. (5)]

$$V_{\nu\nu'}(\beta_1, \beta_2, \dots) = \int \frac{d\boldsymbol{\rho}}{\rho} \phi_\nu^*(\boldsymbol{\rho}) \hat{V}(\boldsymbol{\rho}; \beta_1, \beta_2, \dots) \phi_{\nu'}(\boldsymbol{\rho}). \quad (18)$$

Treating β_i (instead of α_i) as fixed parameters of the Brillouin-Wigner perturbation theory, we finally get rid of the a -dependence in Eq. (15). Thus, Eq. (15) becomes the ordinary eigenvalue problem. The dependence of the spectrum on the physical parameters α_i can be restored by means of inverse functions $\alpha_i = \alpha_i(a; \beta_1, \beta_2, \dots)$. Obviously, such back transformation exists only if there is one-to-one relation between α 's and β 's. In other words, α_i should be a single-valued function. This imposes some additional restrictions on the perturbation \hat{U} . Moreover, the requirement to have bound states in the perturbed spectrum implies the asymptotic behavior $\hat{U}(\mathbf{r}) \rightarrow 0$ at $r \rightarrow \infty$. In the next section we however consider an example of potential which does not satisfy the latter condition.

IV. EXAMPLE: HYDROGEN ATOM IN A STATIC ELECTRIC FIELD

The interaction of an electron with a static electric field $\boldsymbol{\mathcal{E}} = (0, 0, \mathcal{E})$ has the form

$$\hat{U}(\mathbf{r}) = -ze\mathcal{E}. \quad (19)$$

According to Eq. (17), the corresponding dimensionless operator is

$$\hat{V}(\boldsymbol{\rho}; \beta) = -\beta\rho^2 \cos\theta \quad (20)$$

where

$$\beta = \frac{2\mu a^3}{\hbar^2} e\mathcal{E}. \quad (21)$$

The matrix elements $V_{\nu\nu'}$ are calculated in Appendix A. They have simple analytical form and satisfy rigorous selection rules. Namely, only the elements with

$$m' = m, \quad l' = l \pm 1, \quad n' = n, n \pm 1, n \pm 2 \quad (22)$$

are nonvanishing.

As it is already mentioned, the Brillouin-Wigner perturbation theory fails when the perturbation destroys the bound states spectrum. In case of the perturbation Eq. (19), the electric field potential provides a non-zero probability of an electron to tunnel through the local Coulomb barrier. The states become quasi-bound, having nonvanishing imaginary part of the energy. On the other hand, the Rayleigh-Schrödinger perturbation series is Borel summable, having zero radius of convergence.¹⁰ Although the required accuracy can be achieved by sufficient number of perturbation orders taken into account, the higher the accuracy of calculations one wants to approach the smaller should be the region of the field magnitude.

Let's calculate corrections to the electron ground state energy, accounting for only the first few orders of the perturbation theory. As the electron ground state is non-degenerate, the n -th order can be calculated by means of the following recurrent formula¹¹

$$\begin{aligned} \lambda &= \sum_s \lambda^{(s)}, \quad \lambda^{(s)} = \sum_{\nu} V_{0\nu} C_{\nu}^{(s-1)} \\ C_{\nu}^{(0)} &= \delta_{\nu 0}, \quad C_0^{(s)} = 0 \quad (s > 0), \\ C_{\nu}^{(s)} &= \frac{1}{\lambda_{\nu}^{(0)} - \lambda^{(0)}} \left[- \sum_{\nu'} V_{\nu\nu'} C_{\nu'}^{(s-1)} + \sum_{r=1}^{s-1} \lambda^{(r)} C_{\nu}^{(s-r)} \right] \quad (s > 0, \nu > 0), \end{aligned} \quad (23)$$

where the upper script shows the perturbation order in the calculation of the ground state eigenvalue and eigenvector. For simplicity, in eigenvectors and matrix elements $\nu = 0$ denotes the unperturbed ground state; it is omitted in eigenvalues $\lambda^{(s)} \equiv \lambda_0^{(s)}$.

Due to the fact that \hat{V} couples any unperturbed state with only finite number of states, the eigenvalues and eigenvectors of each finite order can be easily calculated analytically. For example, up to the eighth order, the ground state eigenvalue has the form

$$\lambda = 1 - 36 \beta^2 - 20\,052 \beta^4 - 292\,973\,512 \beta^6 - 73\,522\,897\,716 \beta^8 - \dots \quad (24)$$

To return back to the energy and electric field we use Eqs. (2), (4), and (21) that yields an indirect dependence $E(\mathcal{E})$. The numerical plots of the ground state energy measured in

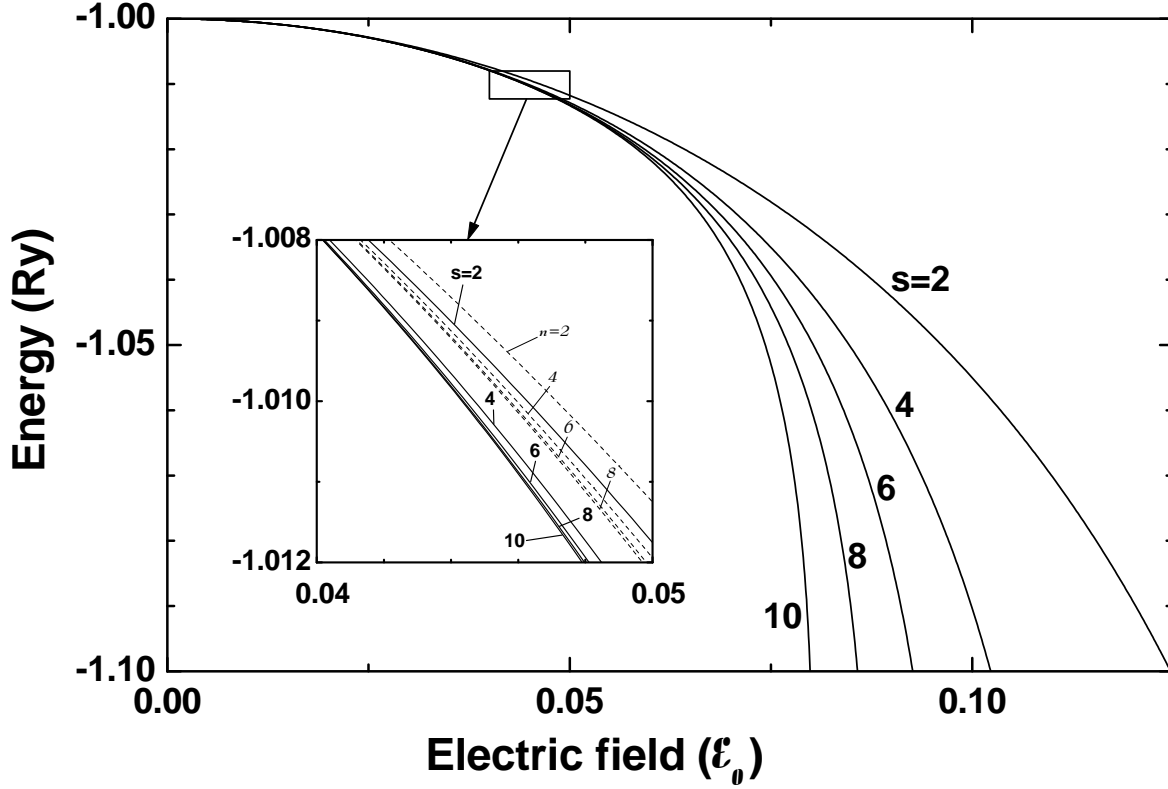


FIG. 1: The ground state electron energy (measured in Rydberg) as a function of the electric field (measured in $\mathcal{E}_0 = a_B^2/e$) calculated via the perturbation theory up to $s = 2, 4, 6, 8$, and 10th order (full curves). The same calculated as a power series of \mathcal{E} up to $n = 2, 4, 6$, and 8th order (dashed curves).

Rydberg versus the electric field strength measured in $\mathcal{E}_0 = a_B^2/e$ are shown in Fig. 1, for different perturbation orders s taken into account. Note that even the curve $s = 2$ is not purely parabolic but contains all orders of \mathcal{E} , since for any finite order E is a transcendental function of \mathcal{E} . Nevertheless, this function can be expressed as a finite series of \mathcal{E} , all higher orders being cut off. Then we result in the known series¹²

$$\frac{E}{\text{Ry}} = -1 - \frac{9}{2} \left(\frac{\mathcal{E}}{\mathcal{E}_0} \right)^2 - \frac{3555}{32} \left(\frac{\mathcal{E}}{\mathcal{E}_0} \right)^4 - \frac{2512779}{256} \left(\frac{\mathcal{E}}{\mathcal{E}_0} \right)^6 - \frac{13012777803}{8192} \left(\frac{\mathcal{E}}{\mathcal{E}_0} \right)^8 - \dots \quad (25)$$

At first glance, this expression gives worse approximation than Eq. (24), since the energies are shifted upwards, see dashed curves in the inset (Fig. 1). On the other hand, neither of these two series is convergent at higher orders and it makes sense only to speak about conditional convergence. As seen from Fig. 1, at $\mathcal{E} > 0.05\mathcal{E}_0$, the series Eq. (24) is not convergent even for the lowest orders $s = 2$ to 10: The discrepancy in the energy calculated in two neighboring perturbation orders does not become notably smaller with every next order. In

reality, the difference between Eq. (24) and Eq. (25) simply estimates the accuracy of the perturbative approach, which, in turn, is of the order of the imaginary part of the complex eigenenergy.¹² At small field strengths such decay rate of the bound electron (exciton) state is rather small and one can get from the perturbation theory a reasonable correction (of the order of several percent) to the bound state energy.

V. DISCUSSION

The new perturbation method formulated in the present paper has a number of advantages compared to the standard perturbation scheme. First of all, it allows to exclude from consideration the continuum states of the unperturbed hydrogen-like problem and, for a large class of perturbations, to reduce the Schrödinger equation to the ordinary eigenvalue problem with equidistant (instead of $-Ry/n^2$) unperturbed spectrum. In particular, the discrete representation of the Coulomb Green's function has the form

$$G_E(\mathbf{r}, \mathbf{r}') = \frac{2\mu a}{\hbar^2} \sum_{nlm} \frac{1}{n - \lambda} \chi_{nlm}^*(\mathbf{r}'; a) \chi_{nlm}(\mathbf{r}; a), \quad E < 0, \quad (26)$$

where $\lambda(E)$ and $a(E)$ are given by Eqs. (4) and (2), respectively. In contrast to the results of Ref. 13 where the Laguerre-Sturmian expansion leads to a tridiagonal form of the Green's operator, the Green's function Eq. (26) has the standard diagonal form with the discrete eigenvalues $\lambda^{(0)} = n$ snading in the denominator.

Second, the use of the energy-dependent parameter a in the expansion of any square integrable function leads to one and the same exponential decay of the basic functions, the correct asymptotic of the expanded function. At the same time, in the standard perturbative methods each basic function has its own asymptotic behavior at $r \rightarrow \infty$ that basically results in a slower convergence compared to the present method.

Third, the matrix elements of the perturbation operator, after it is transformed to the dimensionless form Eq. (17), are very simple and in many cases can be calculated analytically.

Forth, the basic functions support the spherical symmetry that can be very useful when a perturbation also possesses some symmetry. For instance, the perturbative approach to the Stark problem, Sec. IV, is very similar to the solution of the problem in the parabolic coordinates.⁷ However, introducing of the magnetic field into the Hamiltonian, makes the 'parabolic approach' extremely hard, since the basic functions are not the eigenfunction

of the angular momentum operators. Contrarily, in our method, the matrix elements of the electron potential in both electric and magnetic fields have simple analytical form and selection rules.

Fifth, the complete set of functions Eq. (10) can be used for expansion of the wave function even if the Hamiltonian does not contain Coulomb potential. One way to deal with such problems is to add and subtract the Coulomb potential from the Hamiltonian and then follow the present perturbation method. Another way is to expand the wave function of interest into the basis Eq. (10) with constant (energy-independent) parameter a and then diagonalize the Hamiltonian.³ In the latter case it is recommended to treat a as an adjustable parameter.

Acknowledgments

The author is grateful to Roland Zimmermann for helpful advices and frequent discussions. The present work has been inspired by him from the very beginning and it is a special pleasure for the author to contribute to the Festschrift in his honor. Also thanks to S.G. Tikhodeev for critical reading of the manuscript. The work is supported by the Russian Foundation for Basic Research and Russian Ministry of Science (programs “Nanostructures” and “Information Systems”).

Appendix A: Calculation of the matrix elements

The matrix elements of the perturbation \hat{V} , Eq. (20), have the form

$$V_{\nu\nu'} = -\beta \int \frac{d\boldsymbol{\rho}}{\rho} \phi_{\nu}^*(\boldsymbol{\rho}) \rho^2 \cos \theta \phi_{\nu'}(\boldsymbol{\rho}) = -\beta \delta_{mm'} J_{ll'}^m I_{nn'}^{ll'}, \quad (\text{A1})$$

where ($m = 0$)

$$J_{ll'}^0 = \int d\Omega \mathcal{Y}_{l0}(\theta) \cos \theta \mathcal{Y}_{l'0}(\theta) = \frac{\sqrt{(2l+1)(2l'+1)}}{2} \int_{-1}^1 dt t P_l(t) P_{l'}(t), \quad (\text{A2})$$

$$I_{nn'}^{ll'} = \int_0^\infty d\rho y_{nl}(\rho) \rho^2 y_{n'l'}(\rho) = \sqrt{\frac{(n-l-1)!(n'-l'-1)!}{(n+l)!(n'+l')!}} \int_0^\infty e^{-\rho} L_{n-l-1}^{2l+1}(\rho) L_{n'-l'-1}^{2l'+1}(\rho) \rho^{l+l'+3} d\rho. \quad (\text{A3})$$

Using the recurrent relations and orthogonality of the Legendre and Laguerre polynomials, we immediately find

$$J_{l'}^0 = \frac{l+1}{\sqrt{(2l+1)(2l+3)}} \delta_{l+1,l'} + \frac{l}{\sqrt{(2l+1)(2l-1)}} \delta_{l-1,l'}, \quad (\text{A4})$$

$$\begin{aligned} I_{nn'}^{ll+1} = & -\sqrt{(n-l)(n+l+1)(n+l+2)(n+l+3)} \delta_{n+2,n'} \\ & + 2(2n-l) \sqrt{(n+l+1)(n+l+2)} \delta_{n+1,n'} \\ & - 6n \sqrt{n^2 - (l+1)^2} \delta_{n,n'} \\ & + 2(2n+l) \sqrt{(n-l-1)(n-l-2)} \delta_{n-1,n'} \\ & - \sqrt{(n+l)(n-l-1)(n-l-2)(n-l-3)} \delta_{n-2,n'}, \end{aligned} \quad (\text{A5})$$

and

$$I_{nn'}^{ll-1} = I_{n'n}^{l-1l}. \quad (\text{A6})$$

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